168

Extraction of Tannin by Centrifugal Filtration†

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Most vegetable tanning extracts are prepared by countercurrent leaching or percolating of the disintegrated barks, woods or other tannin-containing materials. This process, familiar to most tanners, is described by Wilson[7] and others.

In such a system of leaching, the suitable preparation of the tanning material is of major importance. If the particles are too large, it is difficult to wet them thoroughly and extraction of tannin is slow and incomplete. On the other hand, if much fine powder is present, it tends to pack into a solid

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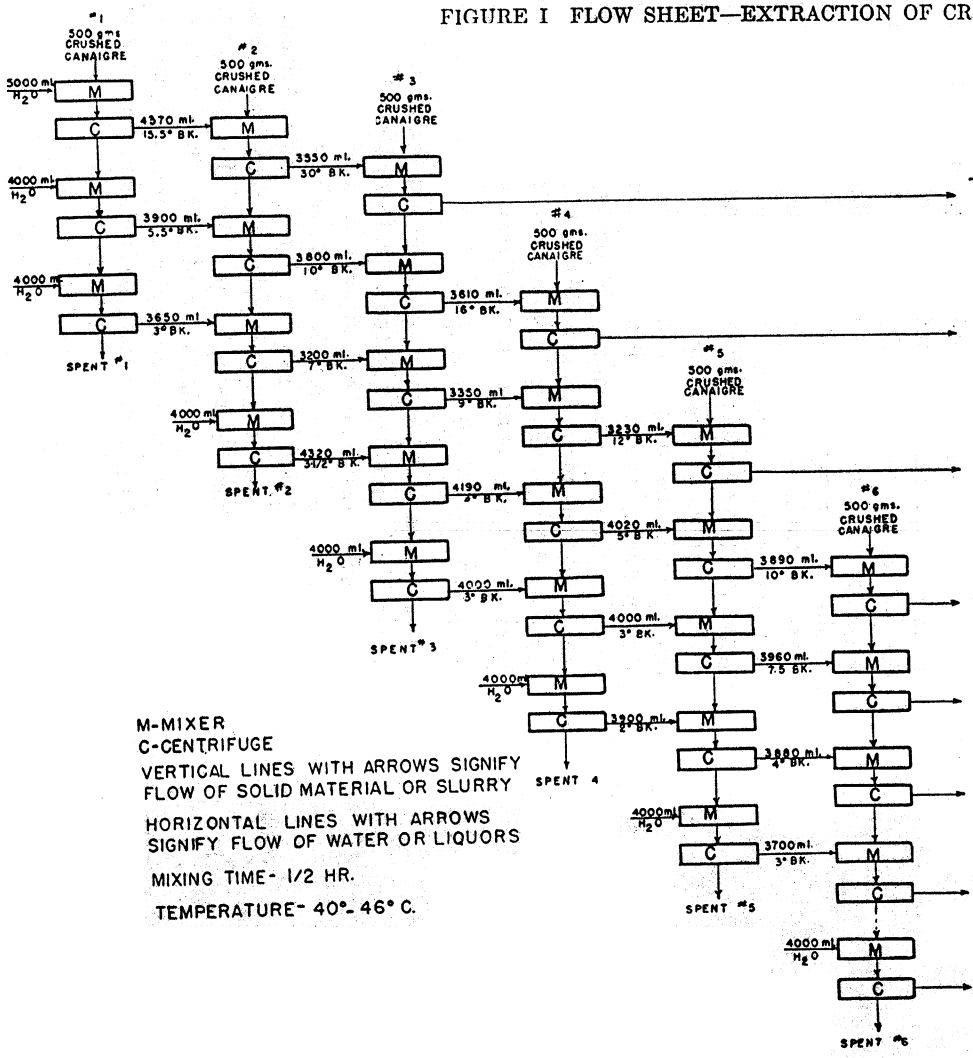
mass, which is also difficult to wet thoroughly. In addition, the fine powder is carried through into the liquors, causing undesirable sediment. The particles produced by the usual types of disintegration equipment, grinders, chippers, hammer mills, etc., in many instances are unsuitable for efficient leaching. These particles range in size from a fine powder to large pieces with 0.5 inch edges. For some materials, especially barks, a sugar cane mill might be used to advantage, as it makes the bark easily permeable to water without forming dust.

In some cases, extraction by percolation becomes difficult, if not impossible, no matter what the state of disintegration of the material. The leaching of tara pods, *Caesalpinia spinosa* (Mol.) Kuntze, is difficult because of the gum in the seeds, which swells in water and clogs the leaches, thus preventing the percolation of the liquors.[4] The starch in canaigre, *Rumex hymenosepalus* Torr., causes difficulty; at temperatures above the gelatinization point of starch, leaching is impossible. Even at moderate temperatures (50-60° C.) the starch granules swell, causing the material to become somewhat slimy and thus interfering with the effective penetration and percolation of the liquor necessary for efficient extraction. Even below 50° C. particle size must be fairly large to permit percolation, and these large particles result in incomplete extraction.

A method has been devised in this laboratory for the efficient extraction of canaigre. This method consists of thorough mixing or agitation of the finely ground or crushed material and separation of the liquor by filtering or centrifuging. While the method has been devised for canaigre, its success with this material has suggested its application for the extraction of other tanning materials. Consequently, tests have been conducted upon several materials under investigation for their possible commercial utilization. These are barks of Pacific Coast hemlock, *Tsuga canadensis;* Florida scrub oak, *Quercus laevis;* and longleaf pine, *Pinus longifolia.* The bark of California tan oak, *Lithocarpus densiflorus,* now being used commercially, was included for comparison.

The method as used in the laboratory consists of either grinding the material in a Wiley mill to pass a one-millimeter screen, or crushing the properly moistened material between stainless steel rolls set at 0.005 inch (0.127 mm.) for canaigre and 0.025 inch (0.635 mm.) for the barks. This crushing results in the formation of sheets or flakes. Portions were weighed into suitable jars immersed in a constant-temperature bath, and the calculated amount of water was added. The mixtures were stirred for one-half hour vigorously enough to prevent any settling. The liquors were then separated from the solid matter in a basket-type centrifuge, in which an 8 inch diameter basket revolving at 3000 to 3500 revolutions per minute was used, and filter press cloth was the filtering medium. Filtration was rapid, but the

FIGURE I FLOW SHEET—EXTRACTION OF CRUSHED CANAIGRE



LIQUOR REMOVED

No.	Vol. Mls.	Density Degrees Barkometer	Total Solids Per Cent	Soluble Solids Per Cent	Insolubles Per Cent	Non Tannin Per Cent	Tannin Per Cent	Purity Tan/Sol. Sds.	Total Solids Gms.	Tannin Gms.
1	3000	48	11.16	10.62	0.54	5.64	4.98	46.9	334.8	149.4
2	3030	32	7.45	7.19	0.26	3.57	3.62	50.3	225.7	109.7
3	2720	31	7.57	7.09	0.48	3.36	3.73	52.6	205.9	101.5
4	3290	26	6.29	5.78	0.51	2.60	3.18	55.0	206.9	104.6
5	3950	11	1.76	1.30	0.46	0.38	0.92	70.8	69.5	36.3
6	3740	7	1.69	0.98	0.71	0.19	0.78	79.6	63.2	29.2
7	3500	4.5	1.23	0.77	0.46	0.12	0.65	84.4	43.1	22.9
8	3950	2.5	0.55	0.35	0.20	0.04	0.31	88.6	21.7	12.2
Total	27,180								1170.8	565.8

necessity of properly balancing the basket required cautious and slow addition of the slurry. The flow sheet for a countercurrent extraction system (Figure I) shows the operation of six extraction vats. In practice, this system would be extended, the second liquor from the sixth vat going to fresh material in the seventh, etc. Since in laboratory tests, six vats were sufficient to give the desired information, the normal operation was suspended after the fourth head liquor had been taken from the sixth vat. To obtain complete data, however, it was necessary that all material be given the number of washes with water required for thorough extraction. Accordingly, the remaining material was given the same treatment that would have been given if the system were in continuous operation, and the weak liquors thus produced were added to the other liquors for analysis.

Analyses were made of the original material, of the spent material, of every liquor removed, of the composite liquors, and of the liquid and powdered extracts prepared from them by evaporation in vacuum. Extracts of canaigre were prepared from a mixture of all liquors remaining after the removal of aliquots for analysis. In tests on the other materials, liquors 2, 3 and 4 were concentrated, since these were more nearly the composition of the liquor that would be obtained in actual practice. The efficiency of extraction was calculated by determining the ratio of the total solids or tannin in the recovered liquors to that in the original material. The total accounted for is the ratio of the sum of the total solids or tannin in the recovered liquors plus that in the spent material to that in the original material. The latter figure is sometimes greater than 100, indicating a recovery of more tannin than was shown by analysis. It is not known whether this result is due to defects in the method of analysis, particularly of the spent material, or to a solubilization during the extracting process of material non-extractable by the analytical method. In commercial leaching under some conditions, more tannin is obtained than is shown by analysis; Belavsky and Wanek[1] reported that 8.38 per cent more tannin was recovered in the extraction of pine bark than was shown by analysis.

Results Obtained with Canaigre

Extractions of canaigre roots have been made under varying conditions of particle size, temperature, time, etc. In addition, tests have been conducted to improve the purity of the extracts produced. These results will be reported at a later date. In the present report only two typical extractions are discussed. Shredded canaigre roots from Sacaton, Arizona were used. In the first test they were crushed in rolls set 0.005 inch apart, and in the second they were ground to pass a 1 mm. screen. In each test they were mixed for one-half hour at a temperature of 40 to 46° C. The extraction procedure and analytical results for crushed canaigre are given in the flow sheet; they are typical of the tests with powdered canaigre as well as with the other

TABLE I

EXTRACTION OF CANAIGRE AT 40-46° C.

	CRUSHED						POWDERED		
	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract	Original Material[1]	Recovered Liquor[2]	Spent Material[1]
Amount used or recovered	2,750 gms.	27,180 mls.	1,402 gms.	.....	.....	.....	1,346 gms.	13,680 mls.	728 gms.
Analyses	.....	18 Bk.	.....	18 Bk.	52 Tw.	.....	.....	16 Bk.	.....
Density—degrees	52.01	4.31	9.36	4.12	51.04	97.29	52.01	3.91	11.50
Total solids—%	45.33	3.86	8.98	4.04	49.28	93.70	45.33	3.65	10.43
Soluble solids—%	6.68	0.55	0.38	0.08	1.76	3.59	6.68	0.26	1.07
Insolubles—%	18.88	1.78	2.86	1.89	23.29	43.96	18.88	1.56	2.20
Non tannin—%	26.45	2.08	6.12	2.15	25.99	49.74	26.45	2.09	8.23
Tannin—%	58.4	53.9	73.2	53.2	52.7	53.1	58.4	57.3	78.9
Purity	.....	82	.....	.....	.....	.....	.....	77	.....
Efficiency of extraction									
Total solids basis—%[3]	.....	78	.....	.....	.....	.....	.....	80	.....
Tannin basis—%[4]	.....	.....	91	.....	.....	.....	.....	.....	88
Total accounted for									
Total solids basis—%[5]	.....	.....	90	.....	.....	.....	.....	.....	97
Tannin basis—%[6]	.....	.....							

[1] Moisture-free basis.
[2] Calculated from analyses of individual liquors.
[3] Ratio of total solids in recovered liquors to those in the original material.
[4] Ratio of tannin in recovered liquors to that in the original material.
[5] Ratio of total solids in recovered liquors plus those in spent material to those in original material.
[6] Ratio of tannin in recovered liquors plus that in spent material to that in original material.

TABLE II

Extraction of Hemlock Bark at 85-100° C.

	CRUSHED						POWDERED					
	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract
Amount used or recovered	1,314 gms.	10,260 mls.	1,034 gms.	.....	.....	.....	1,330 gms.	12,190 mls.	1,083 gms.	.....	.....	.....
Analyses												
Density—degrees....	.....	9 Bk.	.....	17.5 Bk.	25 Tw.	.....	.....	9 Bk.	.....	15 Bk.	31 Tw.	.....
Total solids—%.....	26.18	2.44	6.27	4.38	28.96	97.46	27.46	2.52	5.85	4.26	36.22	96.35
Soluble solids—%....	22.00	2.10	5.37	3.79	25.74	82.41	23.96	2.24	4.93	3.58	32.30	85.78
Insolubles—%.....	4.18	0.34	0.90	0.59	3.22	15.05	3.50	0.28	0.92	0.68	3.92	10.57
Non tannin—%.....	8.08	0.80	2.29	1.46	10.30	31.34	8.46	0.78	2.47	1.24	11.16	29.65
Tannin—%.....	13.92	1.30	3.08	2.33	15.44	51.07	15.50	1.46	2.46	2.34	21.14	56.13
Purity.....	63.3	61.9	57.4	61.5	59.8	62.0	64.7	65.2	49.9	65.4	65.4	65.4
Efficiency of extraction												
Total solids basis—%[3]	.....	73	.....	.....	.....	.....	.....	84	.....	.....	.....	.....
Tannin basis—%[4]....	.....	73	.....	.....	.....	.....	.....	86	.....	.....	.....	.....
Total accounted for												
Total solids basis—%[5]	.....	.....	92	.....	.....	.....	.....	.....	102	.....	.....	.....
Tannin basis—%[6]....	.....	.....	90	.....	.....	.....	.....	.....	99	.....	.....	.....

1 Moisture-free basis.
[2]Calculated from analyses of individual liquors.
[3] Ratio of total solids in recovered liquors to those in the original material.
[4] Ratio of tannin in recovered liquors to that in the original material.
[5] Ratio of total solids in recovered liquors plus those in spent material to those in original material.
[6] Ratio of tannin in recovered liquors plus that in spent material to that in original material.

TABLE III

Extraction of Florida Scrub Oak Bark at 85-100° C.

	CRUSHED						POWDERED					
	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract
Amount used or recovered	1,316 gms.	17,590 mls.	1,073 gms.	.....	.....	.....	1,378 gms.	13,120 mls.	1,123 gms.	.....	.....	.....
Analyses												
Density—Degrees....	.....	4 Bk.	.....	5.5 Bk.	30 Tw.	.....	.....	6 Bk.	.....	9.5 Bk.	26 Tw.	.....
Total solids—%.....	18.48	1.17	4.16	1.38	34.60	96.39	17.87	1.70	3.66	2.53	30.92	95.69
Soluble solids—%....	16.78	1.09	3.63	1.30	32.60	91.05	16.54	1.61	3.15	2.42	29.51	90.69
Insolubles—%.....	1.70	0.08	0.53	0.08	2.00	5.34	1.33	0.09	0.51	0.11	1.41	5.00
Non tannin—%.....	6.17	0.34	1.64	0.41	10.73	30.20	6.20	0.52	1.65	0.78	9.47	29.57
Tannin—%.....	10.61	0.75	1.99	0.89	21.87	60.85	10.34	1.09	1.50	1.64	20.04	61.12
Purity.....	63.2	68.8	54.8	68.5	67.1	66.8	62.5	67.7	47.6	67.8	67.9	67.4
Efficiency of extraction												
Total solids basis—%[3]	.....	85	.....	.....	.....	.....	.....	91	.....	.....	.....	.....
Tannin basis—%[4]....	.....	95	.....	.....	.....	.....	.....	100	.....	.....	.....	.....
Total accounted for												
Total solids basis—%[5]	.....	.....	103	.....	.....	.....	.....	.....	107	.....	.....	.....
Tannin basis—%[6]....	.....	.....	110	.....	.....	.....	.....	.....	112	.....	.....	.....

[1] Moisture-free basis.
Calculated from analyses of individual liquors.
[3] Ratio of total solids in recovered liquors to those in the origina material.
[4] Ratio of tannin in recovered liquors to that in the original material.
[5] Ratio of total solids in recovered liquors plus those in spent material to those in original material.
[6] Ratio of tannin in recovered liquors plus that in spent material to that in original material.

materials. Table I shows the analyses of the composite liquors and of the extracts prepared from them, as well as leaching efficiencies with crushed and powdered roots. It will be noted that the efficiency of extraction of tannin is greater for powdered than for crushed material. Several leaching tests conducted in the laboratory under conditions comparable to those used in practice gave efficiencies of only 40 to 50 per cent.

Pacific Coast Hemlock Bark

This bark is available in large quantities on the Pacific Coast, but freight rates to tanning centers near the Atlantic seaboard make its economic utilization doubtful. The current practice of floating logs in mill ponds before removal of the bark results in the loss of one-half of the tannin and also in lowering the quality of the extract. As this bark is not satisfactory for the preparation of tanning extract, woods-peeled bark was used in our tests. For the first test, the bark was crushed between rollers set 0.025 inch apart; for the second test, it was ground to pass a 1 mm. screen. Tests were run as indicated by the flow sheet for canaigre except that for this material and others subsequently tested only one-half the quantity of bark and water was used and the extraction temperatures were 100° C. on the two tail vats and 85 to 90° C. on the other three. Results are shown in Table II. It will be seen that again the ground material gave greater leaching efficiency than the crushed. The figures given for satisfactory leaching of hemlock bark by G. A. Kerr[2] are 75 to 80 per cent. Sands[5] reported an efficiency for Lake States hemlock bark of approximately 73 per cent. The figure for crushed hemlock bark in our test was about equal to that obtained in practice, and that for the powdered bark was considerably higher.

Florida Scrub Oak Bark

These trees grow in considerable quantities in Florida and other southern states. Owing to their small size and comparatively low tannin content, it would be necessary to harvest and debark by cheap and mechanical methods and to utilize by-products if this material were to be successfully used on a commercial scale. Preliminary results along these lines appear promising.

A leaching efficiency of 80 to 85 per cent for oak bark is considered satisfactory by Kerr.[2] Table III shows that the present method has increased the efficiency of extraction to 93.3 per cent for crushed bark and 100 per cent for powdered bark. These results illustrate the previously mentioned effect of obtaining more tannin than is accounted for by analysis.

California Tan Oak Bark

Table IV shows that the method reported here gives greater efficiencies of extraction than do current leaching methods and that the powdered bark is superior to the crushed bark.

TABLE IV

Extraction of California Tan Oak Bark at 85-100° C.

	CRUSHED						POWDERED					
	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract
Amount used or recovered	1,338 gms.	10,240 mls.	896 gms.	.....	.....	.....	1,369 gms.	10,250 mls.	900 gms.	.....	.....	.....
Analyses												
Density—degrees....	.....	15 Bk.	.....	24.5 Bk.	28 Tw.	.....	.....	16 Bk.	.....	30 Bk.	36 Tw.	.....
Total solids—%.....	34.16	3.87	4.77	6.22	31.28	.....	34.62	4.24	3.98	7.46	39.27	91.27
Soluble solids—%....	29.67	3.39	4.16	5.41	27.99	.....	30.59	3.84	3.41	6.71	37.00	85.25
Insolubles—%.....	4.49	0.48	0.61	0.81	3.29	.....	4.03	0.40	0.57	0.75	2.27	6.02
Non tannin—%.....	11.63	1.37	2.06	2.22	11.09	.....	12.16	1.51	1.73	2.61	14.97	34.99
Tannin—%.....	18.04	2.02	2.10	3.19	16.90	.....	18.43	2.33	1.68	4.10	22.03	50.26
Purity.....	60.8	59.6	50.5	59.0	60.4	.....	60.3	60.7	49.3	61.1	59.5	59.0
Efficiency of extraction												
Total solids basis—%[3]	.....	87	.....	.....	.....	.....	.....	92	.....	.....	.....	.....
Tannin basis—%[4]....	.....	86	.....	.....	.....	.....	.....	95	.....	.....	.....	.....
Total accounted for												
Total solids basis—%[5]	.....	.....	96	.....	.....	.....	.....	.....	99	.....	.....	.....
Tannin basis—%[6]....	.....	.....	94	.....	.....	.....	.....	.....	101	.....	.....	.....

[1] Moisture-free basis.
[2] Calculated from analyses of individual liquors.
[3] Ratio of total solids in recovered liquors to those in the origina lmaterial.
[4] Ratio of tannin in recovered liquors to that in the original material.
[5] Ratio of total solids in recovered liquors plus those in spent material to those in original materia
[6] Ratio of tannin in recovered liquors plus that in spent material to that in original material.

Longleaf Pine Bark

This material is available in large quantities in some southern states as a by-product of the pulping industry. Although the bark would thus be inexpensive, the low tannin content makes its economic utilization doubtful. By usual leaching practices, it is difficult to obtain a leaching efficiency greater than 50 per cent. Several European workers[3, 6] have found that a preliminary solvent extraction of pine bark to remove resins or an extraction with a solution of sodium sulfite and bisulfite improves leaching efficiency. Preliminary tests in this laboratory have shown that extraction with such a mixture of sulfite and bisulfite removes more tannin than is shown to be present by analysis. This is due to the solubilizing effect of this solution.

For our test, only the powdered material was available. The extraction method was the same as that used for the other bark samples, except that a dilute solution of a mixture of sodium sulfite and sodium bisulfite in equal proportions (3 per cent solid chemicals, based on the weight of the bark) was used for leaching instead of water. The results are shown in Table V. The tannin recovery was 118 per cent of that shown by analysis of the original material. It is planned to make further studies of this method on a scale large enough for laboratory tanning tests.

TABLE V

EXTRACTION OF LONGLEAF PINE BARK AT 85-100° C.

			POWDERED			
	Original Material[1]	Recovered Liquor[2]	Spent Material[1]	Liquor for Concentration	Liquid Extract	Powdered Extract
Amount used or recovered	1,335 gms.	11,700 mls.	1,080 gms.	.....	.....	.....
Analyses						
Density—degrees	.....	10 Bk.	.....	15 Bk.	42 Tw.	.....
Total solids—%	17.27	2.21	8.40	3.14	39.61	98.95
Soluble solids—%	14.51	1.94	7.96	2.98	37.36	92.76
Insolubles—%	2.76	0.27	0.44	0.16	2.25	6.19
Non tannin—%	7.18	0.96	4.78	1.39	17.91	43.29
Tannin—%	7.33	0.98	3.18	1.59	19.45	49.47
Purity	50.5	50.5	40.0	53.4	52.1	53.3
Efficiency of extraction						
Total solids basis—%[3]	.....	112	.....	.....	.....	.....
Tannin basis—%[4]	.....	118	.....	.....	.....	.....
Total accounted for						
Total solids basis—%[5]	.....	.....	151	.....	.....	.....
Tannin basis—%[6]	.....	.....	153	.....	.....	.....

[1] Moisture-free basis.
[2] Calculated from analyses of individual liquors.
[3] Ratio of total solids in recovered liquors to those in the original material.
[4] Ratio of tannin in recovered liquors to that in the original material.
[5] Ratio of total solids in recovered liquors plus those in spent material to those in original material
[6] Ratio of tannin in recovered liquors plus that in spent material to that in original material.

Discussion

Although in the laboratory tests the materials were mixed by ordinary stirrers and the liquors were separated from the solid materials by means of a centrifuge, the method is not limited to these devices. Satisfactory results have been obtained with a mixer which disintegrates while mixing, thus making unnecessary the preliminary grinding treatment. It might be desirable to substitute a continuous filter, such as the Oliver, for the centrifuge.

The proposed method would require equipment in addition to that in present use in extract plants for grinding, mixing and centrifuging, but on the other hand, it would not require the leach vats or autoclaves. The shorter time required would increase the capacity of the plant. Moreover, the method would result in more economical production because of its increased efficiency. It would also produce extracts of higher quality, as a long extraction process impairs the quality of tanning extracts. The determination of relative costs will require pilot-scale studies. Such tests are being planned.

Summary

A method of extracting tannin from tanning materials has been devised which increases the yield of tannin and the speed of extraction, as compared with usual leaching methods. It includes thorough mixing or agitation of the finely ground or crushed material with water and the separation of the liquor from the solids by filtering or centrifuging. The method is particularly adapted to canaigre, which is difficult to leach by usual procedures. It also apparently gives good results with other tanning materials. Determination of cost figures awaits pilot-scale tests.

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